FMM methods for speeding up the evaluation of Coulombic interactions in QM/MM type calculations

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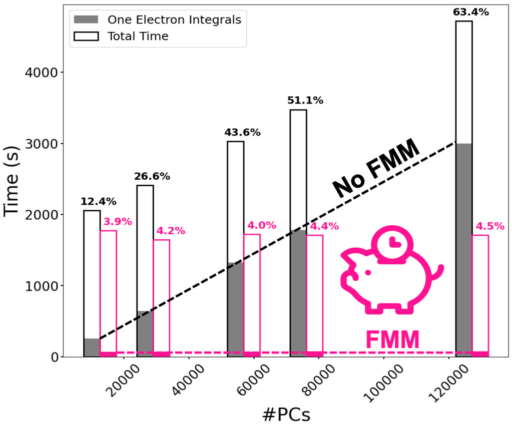

Electrostatic embedded cluster (ECM) methods have proven highly effective for modeling semiconductors and insulators, focusing quantum mechanical (QM) calculations on a central cluster while embedding it in a field of point charges (PCs) that approximate the surrounding environment. A surrounding shell of effective core potentials (ECPs) is used to prevent overpolarization of the QM region. This hybrid approach, when combined with accurate quantum chemistry methods, has successfully captured key electronic and magnetic properties of oxide surfaces under catalytic oxidation conditions.

As research progresses toward modeling surface electrocatalysis under operando conditions with atomistic resolution, the need arises for significantly larger QM clusters, typically 200–300 atoms, and electrostatic environments involving up to a million point charges. At this scale, evaluating the electrostatic potential generated by the PCs becomes a major computational bottleneck, with a cost that scales as $O(N_{PC} \times N_{BF}^2)$, where N_{PC} is the number of point charges and N_{BF} the number of basis functions.

To overcome this bottleneck, we implemented the Fast Multipole Method (FMM) within the ORCA quantum chemistry package. FMM is a hierarchical algorithm that efficiently computes long-range Coulombic interactions by decomposing them into near-field and far-field contributions. Our initial focus on PC–PC and QM–PC electrostatics enabled us to realize substantial speedups, up to 10–100× depending on system size, while maintaining micro-Hartree accuracy.

Particular attention was given to the accurate representation of the electronic density in the far field, for which we developed a multipole expansion scheme that integrates smoothly into the atomic orbital basis framework. We also revisited the partitioning of shell pairs to optimize the near-/far-field split, allowing the FMM to be applied robustly across a wide variety of chemical systems, including slab-like models common in surface chemistry.

Although our primary emphasis is on accelerating Coulomb interactions between QM and MM regions, the long-term objective was to extend FMM to fully cover QM-QM Coulomb terms in large systems. To address this, we developed a new algorithm called RI-BUPO-J ("Bubblepole"). This method combines the resolution-of-identity (RI) approximation with a novel alternative to FMM's hierarchical boxing: adaptive spherical groupings of basis and auxiliary functions ("bubbles"). RI-BUPO-J provides a flexible and intuitive framework for evaluating Coulomb matrices in large systems. It achieves micro- to nano-Hartree accuracy compared to the Split-RI-J reference method, even for systems containing around 1000 atoms. While Split-RI-J remains the fastest approach for compact 3D molecules and linear systems with up to 300–400 atoms, RI-BUPO-J offers a scalable and competitive alternative for large or non-standard systems.

References

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